

Figure 16.1 The products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings

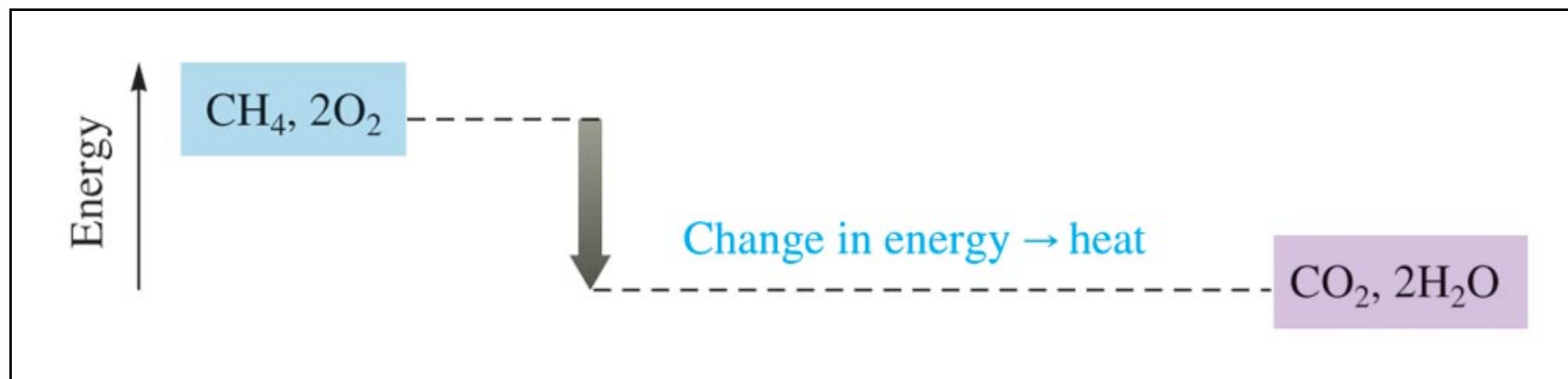
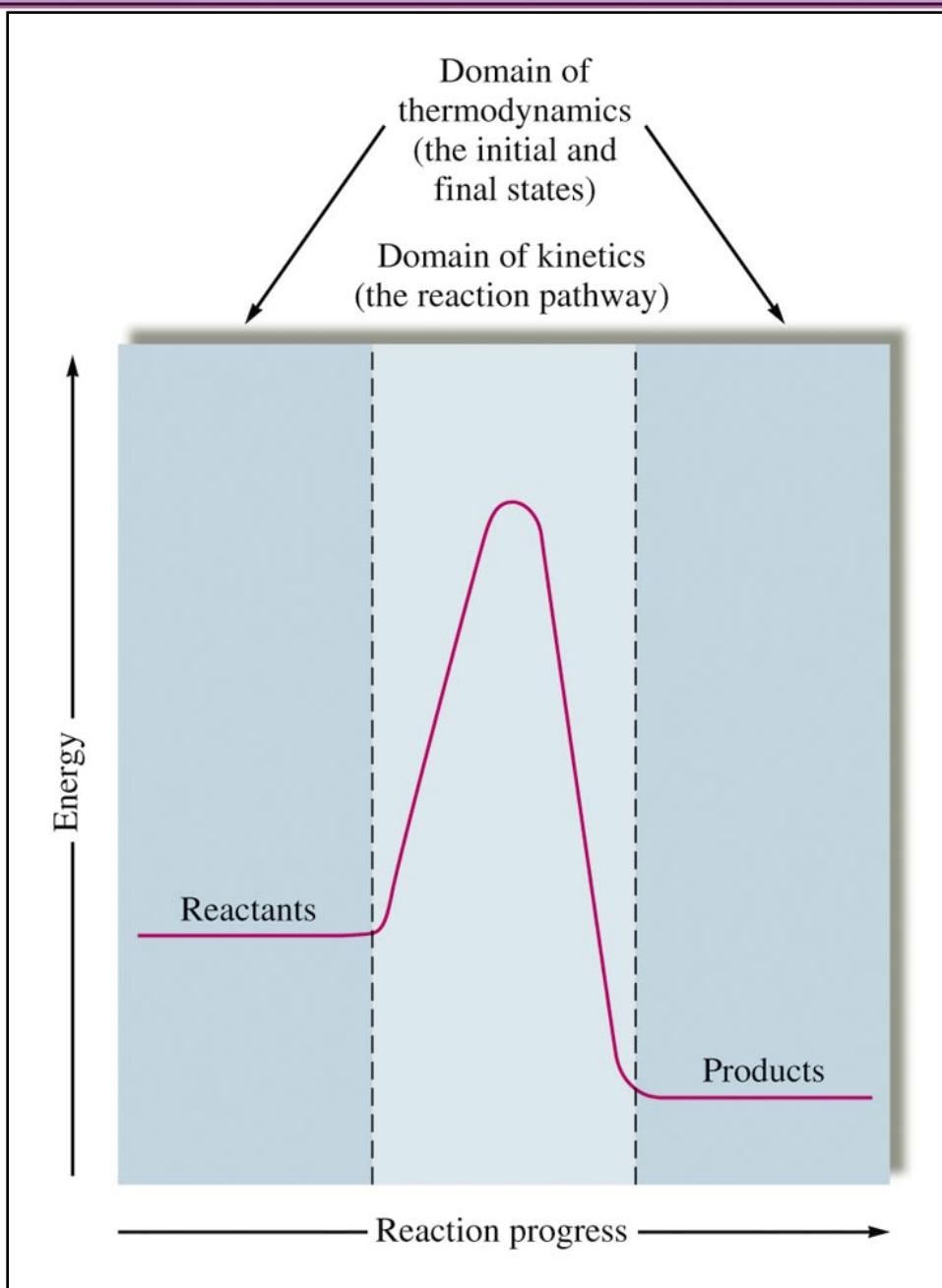


Figure 16.2

Thermodynamics domain



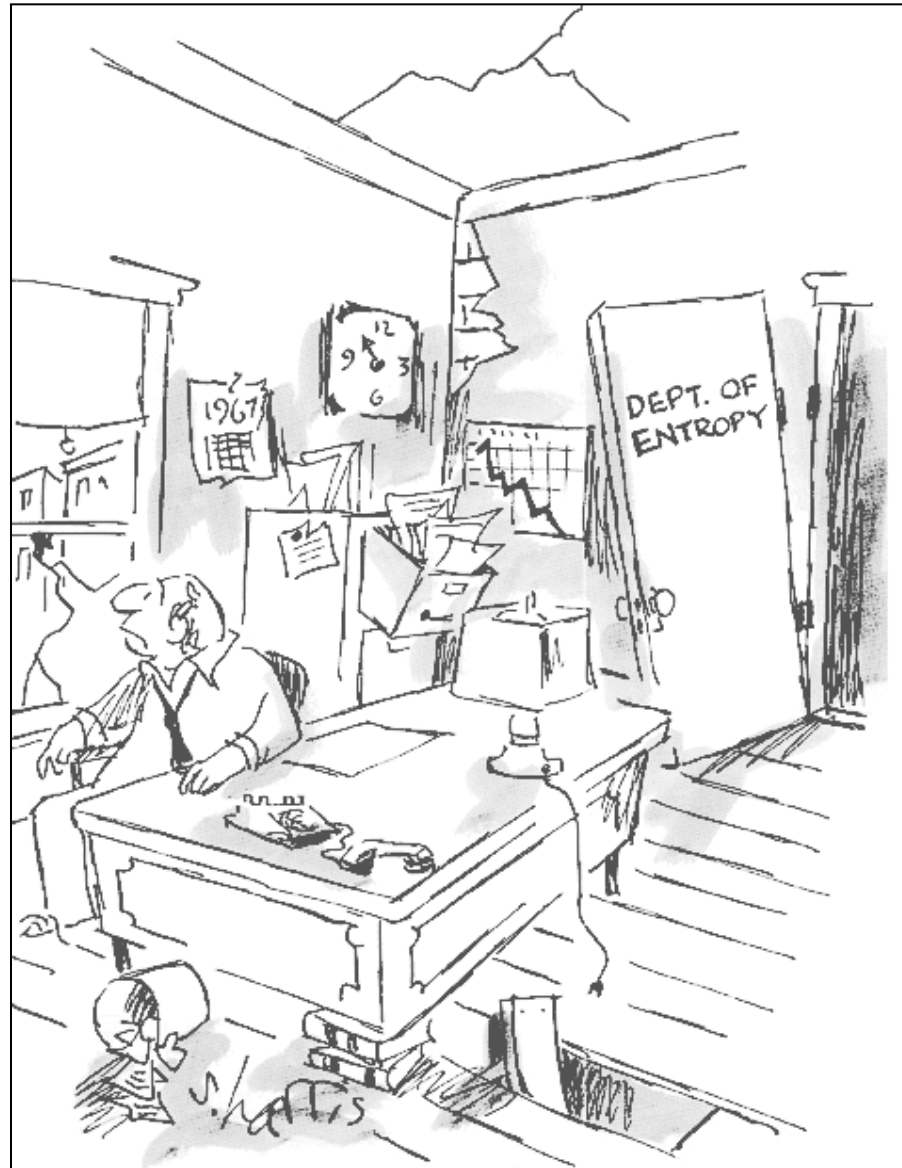


Figure 16.3 The expansion of an ideal gas into an evacuated bulb.

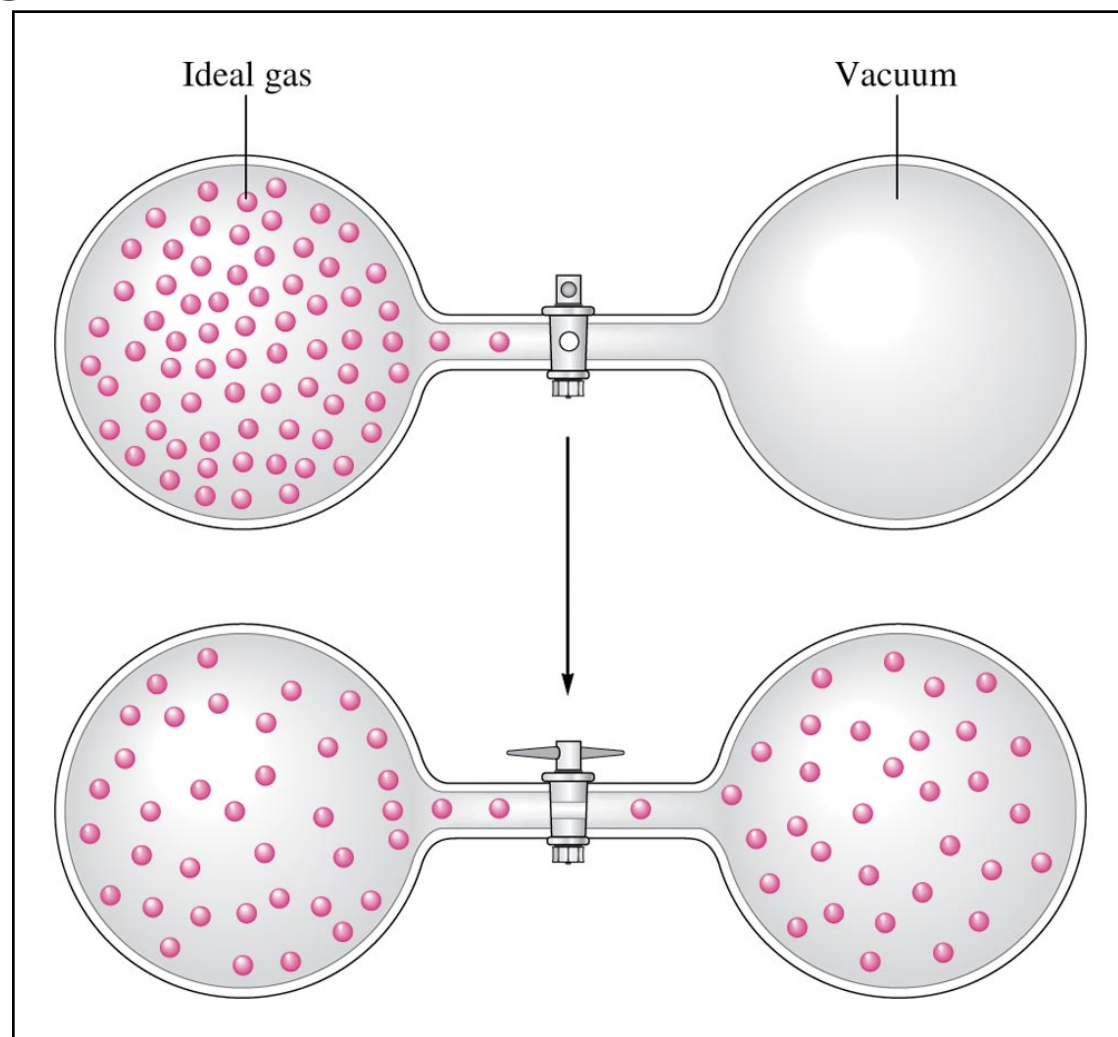


Figure 16.4 Possible arrangements (states) of four molecules in a two-bulbed flask. Numbers indicate available microstates.

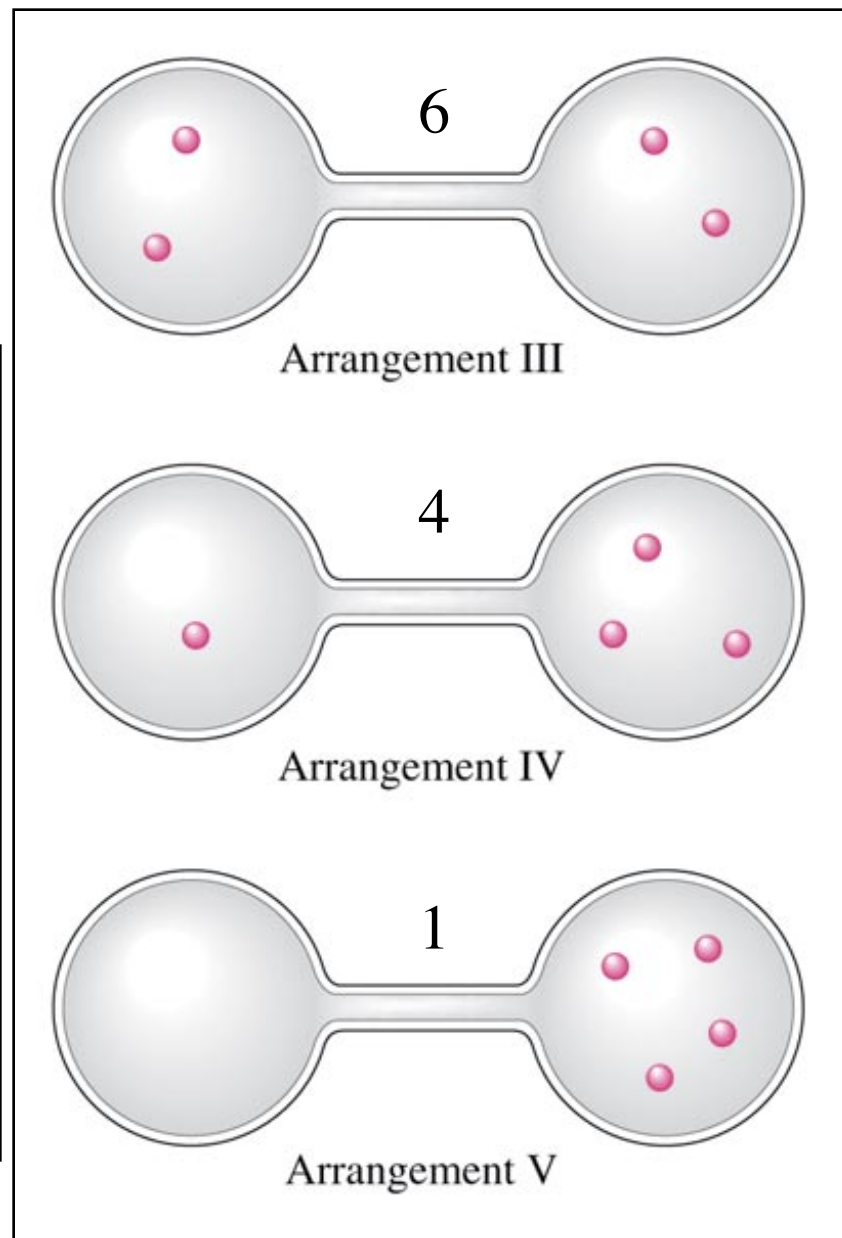
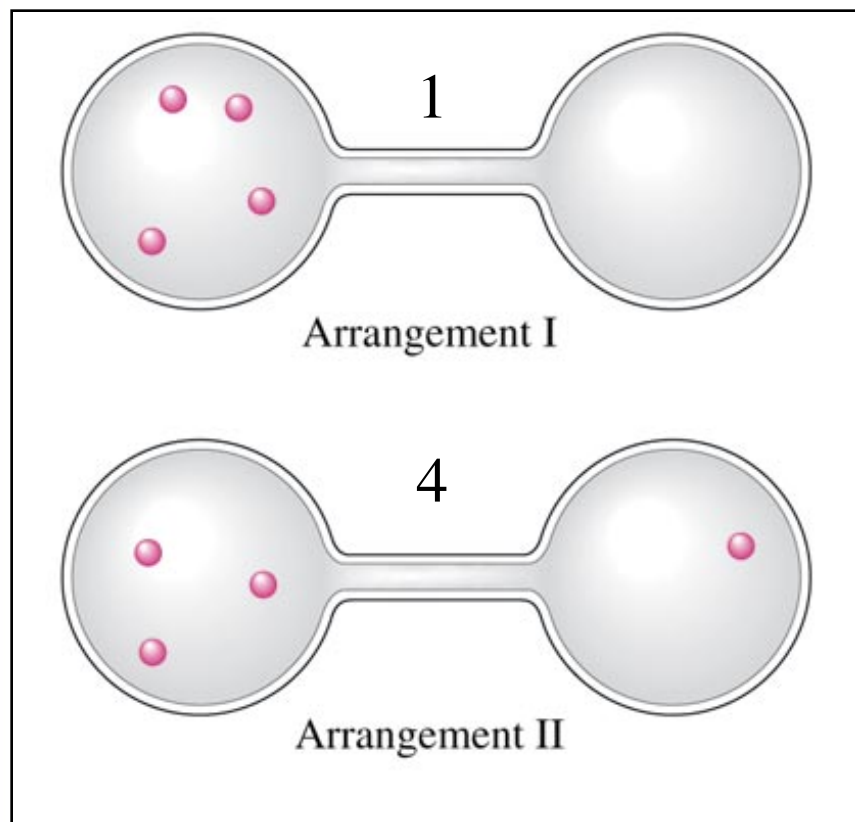


Table 16.1 The Microstates That Give a Particular Arrangement (State)

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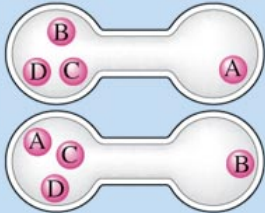
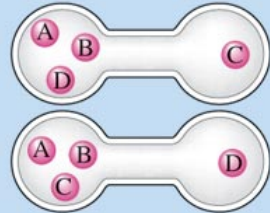
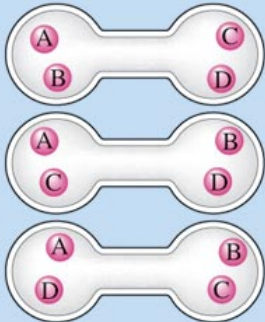
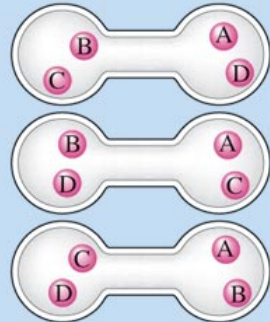
Arrangement	Microstates	
I		
II	 	
III	 	

Table 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

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Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

Probabilities of microstate processes.

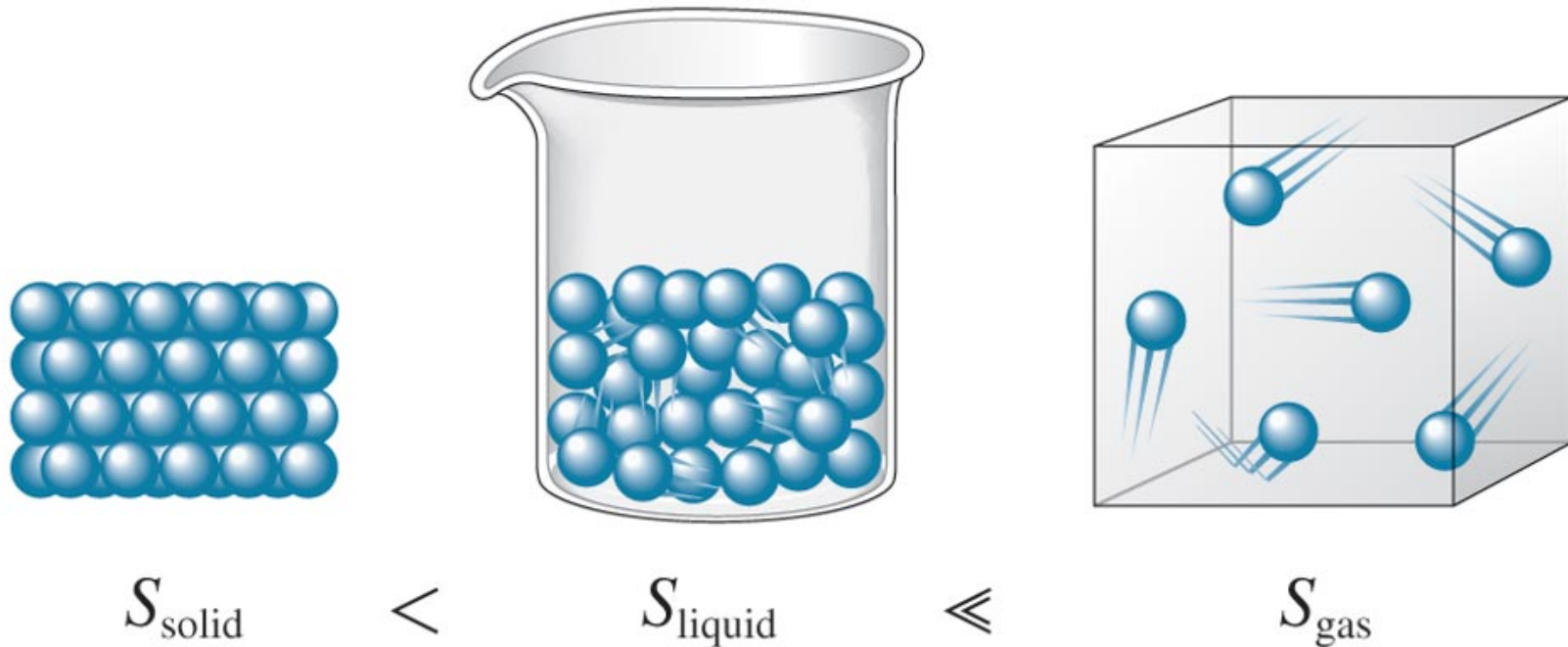


Table 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

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Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	<i>Process Spontaneous?</i>
+	+	+	Yes
—	—	—	No (reaction will occur in opposite direction)
+	—	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
—	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Table 16.4 Results of the Calculation of ΔS_{univ} and ΔG° for the Process $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$ at -10°C , 0°C , and 10°C

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T ($^\circ\text{C}$)	T (K)	ΔH° (J/mol)	ΔS° (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	+0.8	6.25×10^3	-2.2×10^2

*Note that at 10°C , ΔS° (ΔS_{sys}) controls, and the process occurs even though it is endothermic. At -10°C , the magnitude of ΔS_{surr} is larger than that of ΔS° , so the process is spontaneous in the opposite (exothermic) direction.

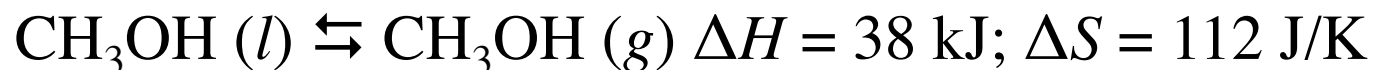
Table 16.5 Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

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Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

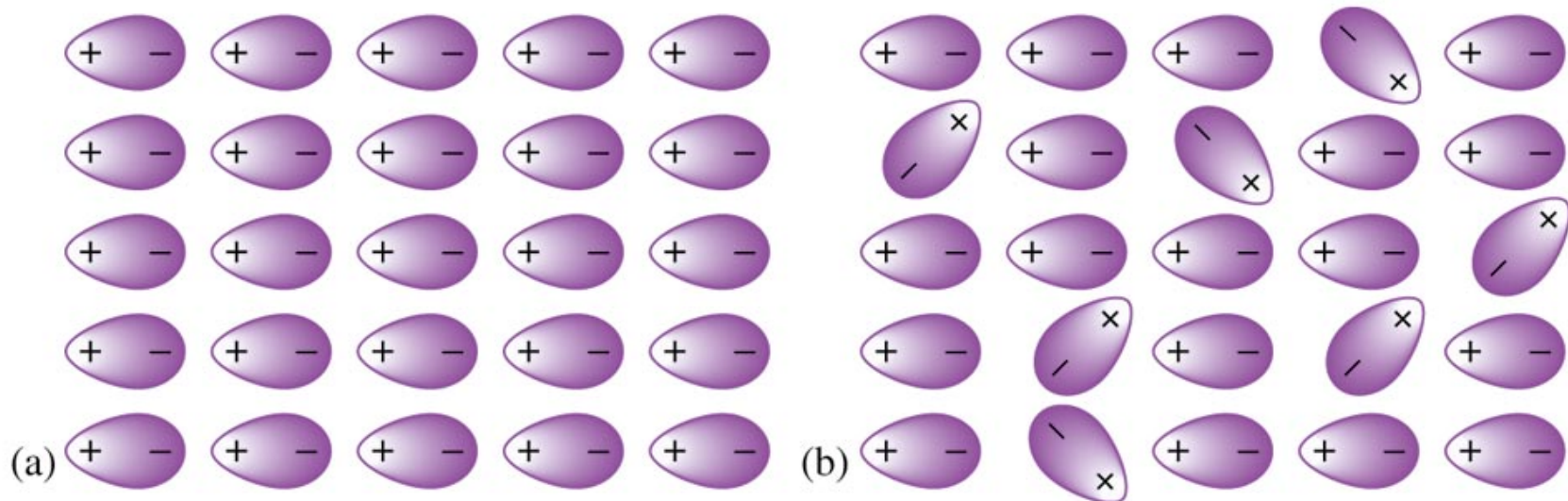
QUESTION

When rubbing alcohol, gasoline, or water vaporizes from your skin you may feel a cooling sensation. At what temperature would the endothermic process of methanol liquid becoming methanol gas reach an equilibrium? Assume one atmosphere of pressure.



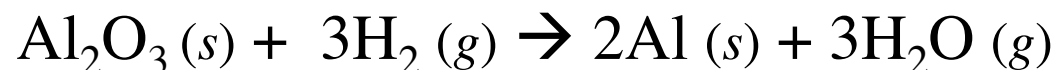
Answer = 63°C

Figure 16.5 a-b The entropy of a perfect crystal at 0K is zero. As the temperature is raised, entropy increases.



QUESTION

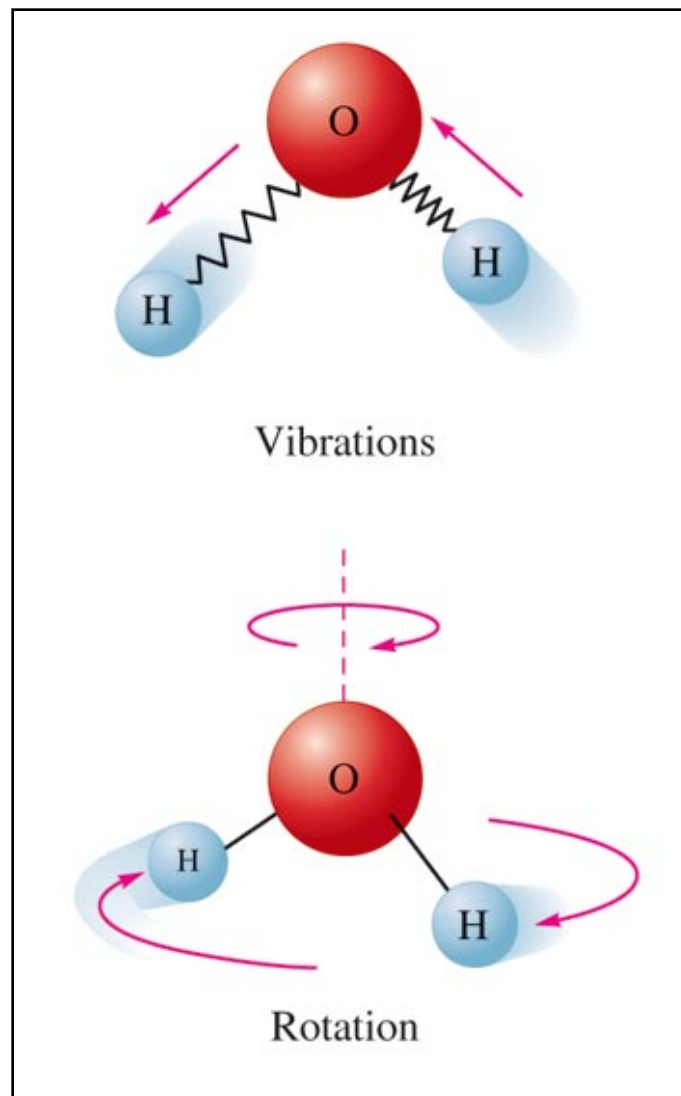
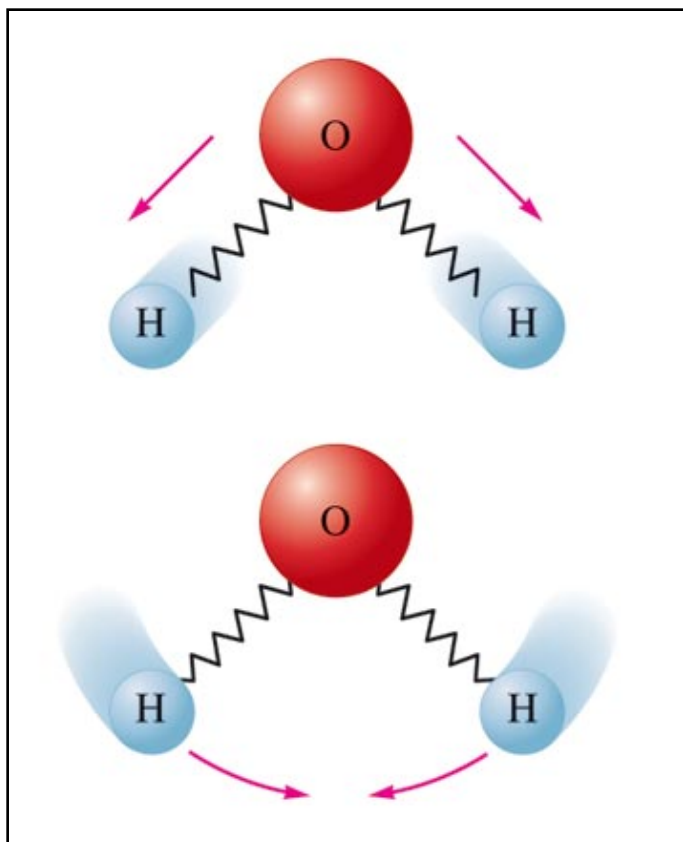
Calculate the ΔS° value for the reduction of aluminum oxide by hydrogen gas using standard entropy values.



Answer = 179 J/K

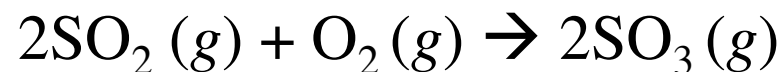
Why so big when 3 mol of gas on both sides?

Figure 16.6 a-d H_2O has rotational and Vibrational motions.

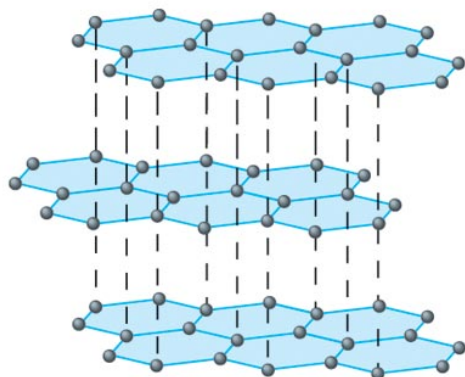


QUESTION

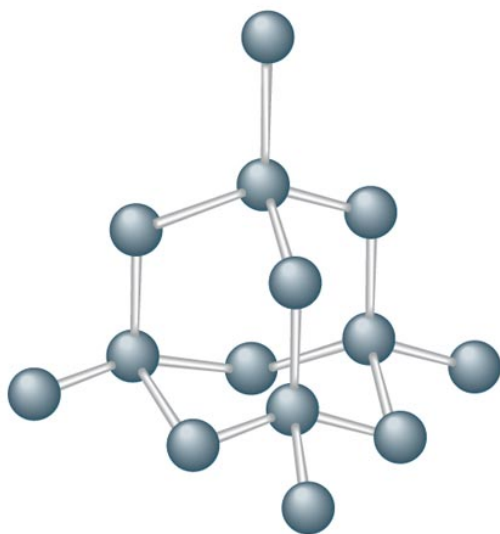
How many ways can you calculate ΔG° ? Calculate ΔG° for the the following reaction in each of those ways.



Answer = -142 kJ

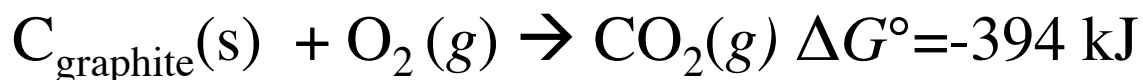
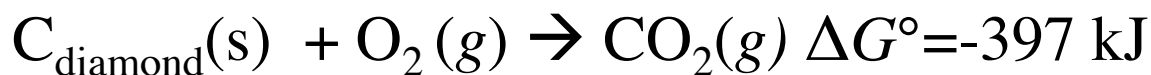


Graphite

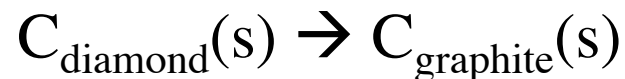


Diamond

Use the following data at 25°C:



Calculate ΔG° for the reaction:



Answer = -3 kJ

Diamonds are Kinetically Stable;
Not Thermodynamically Stable

QUESTION

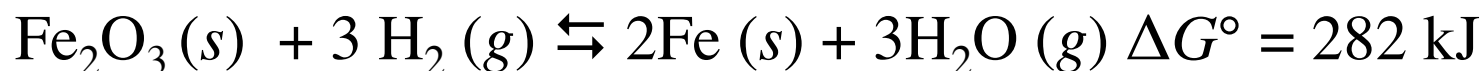
Replacing rusted iron accounts for approximately 20% of our yearly production of steel. The following reaction shows the oxidation of iron metal to iron (III) oxide. The ΔH value for the reaction is -1650 kJ . $\Delta S = -543 \text{ J/K}$. At 25.0°C what is the value for ΔG ?



Answer = -1490 kJ

QUESTION

Adding H_2 gas to hematite ore (Fe_2O_3) under some conditions can produce pure iron. The reaction is



What is the value of ΔG when the temperature is 25.0°C , the pressure of $\text{H}_2 = 3.00 \text{ atm}$, and the pressure of water is 0.0394 atm ?

Answer = 250 kJ

Figure 16.7 a-b Like the Ball, a Chemical System will Seek the Lowest Possible Free Energy (which is Equilibrium)

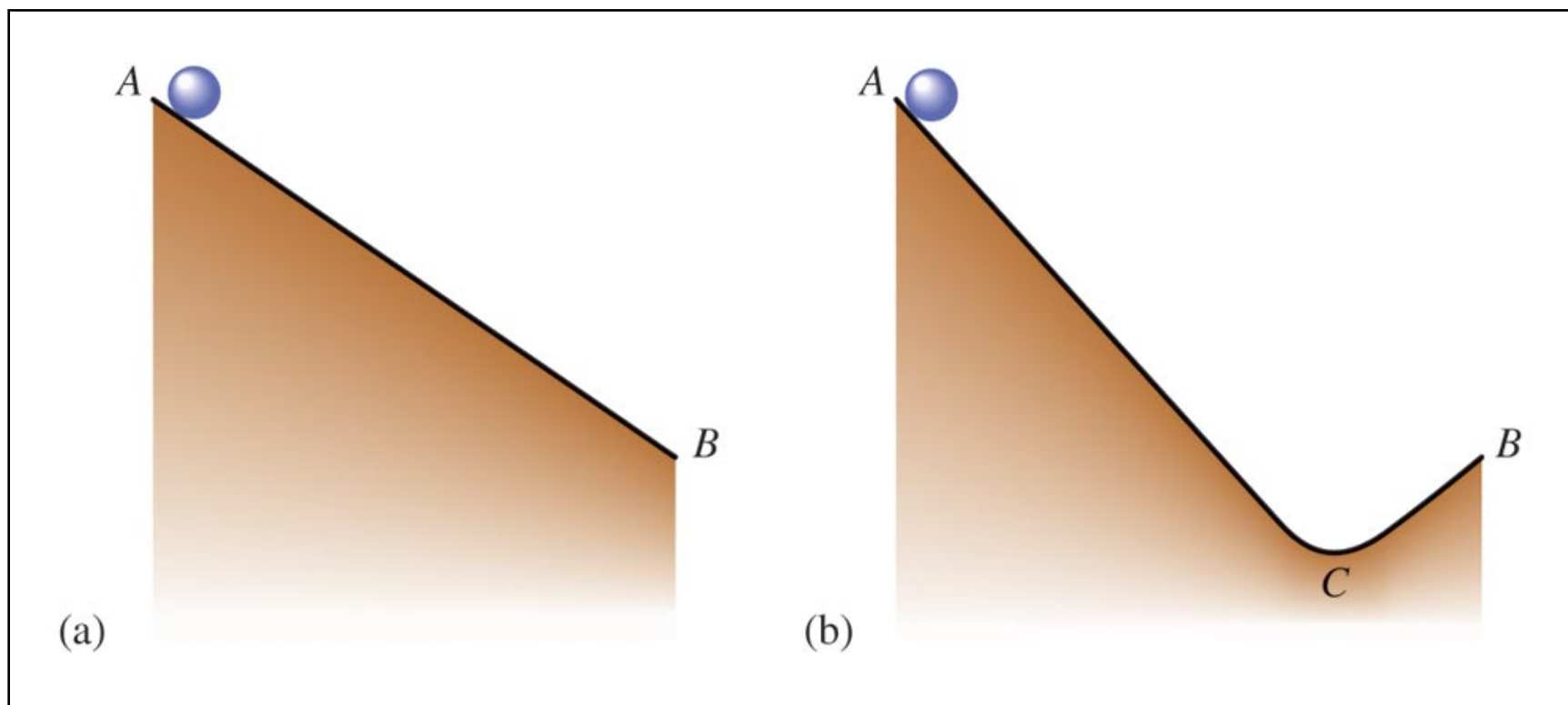


Figure 16.8 a-c
Rxn of $A(g) \rightleftharpoons B(g)$

(a) The initial free energies of A and B.

(b) As $A(g)$ changes to $B(g)$, the free energy of A decreases and that of B increases.

(c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position

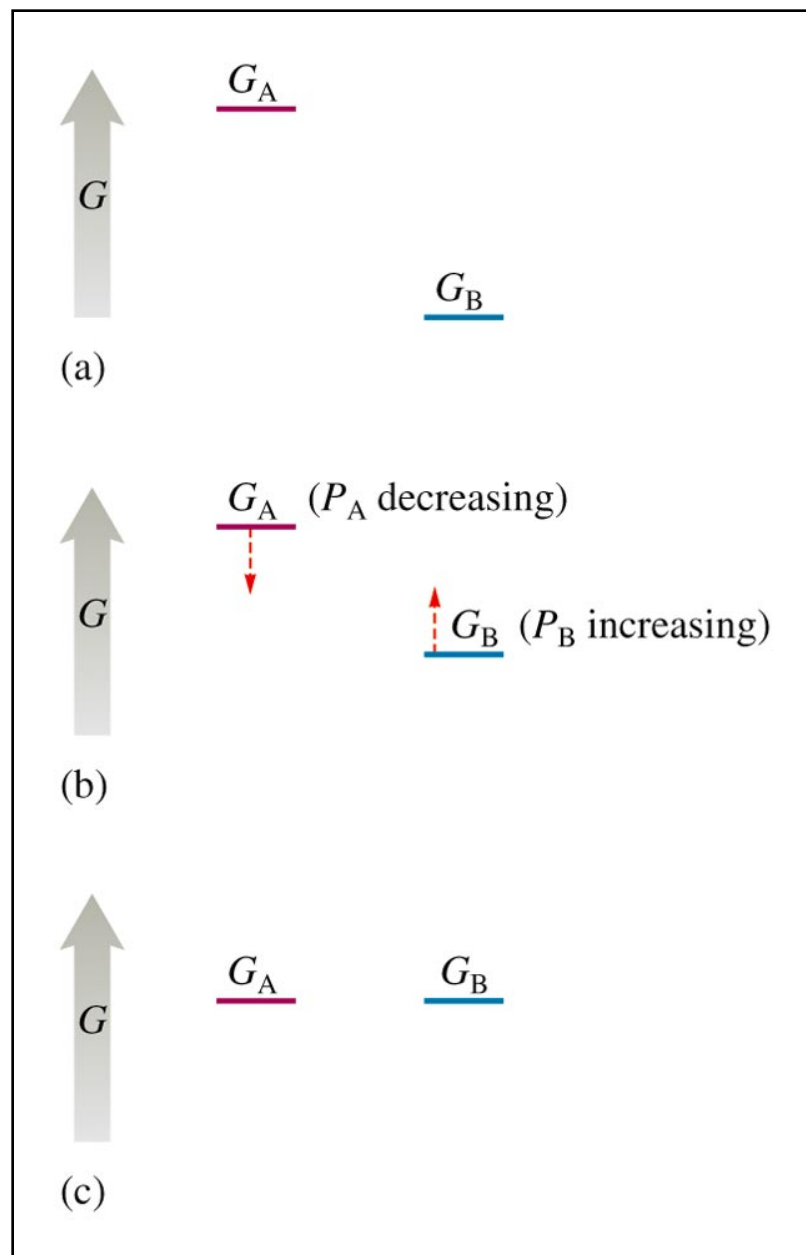


Figure 16.9 a-c Minimum free energy is reached when 75% of A has been changed to B

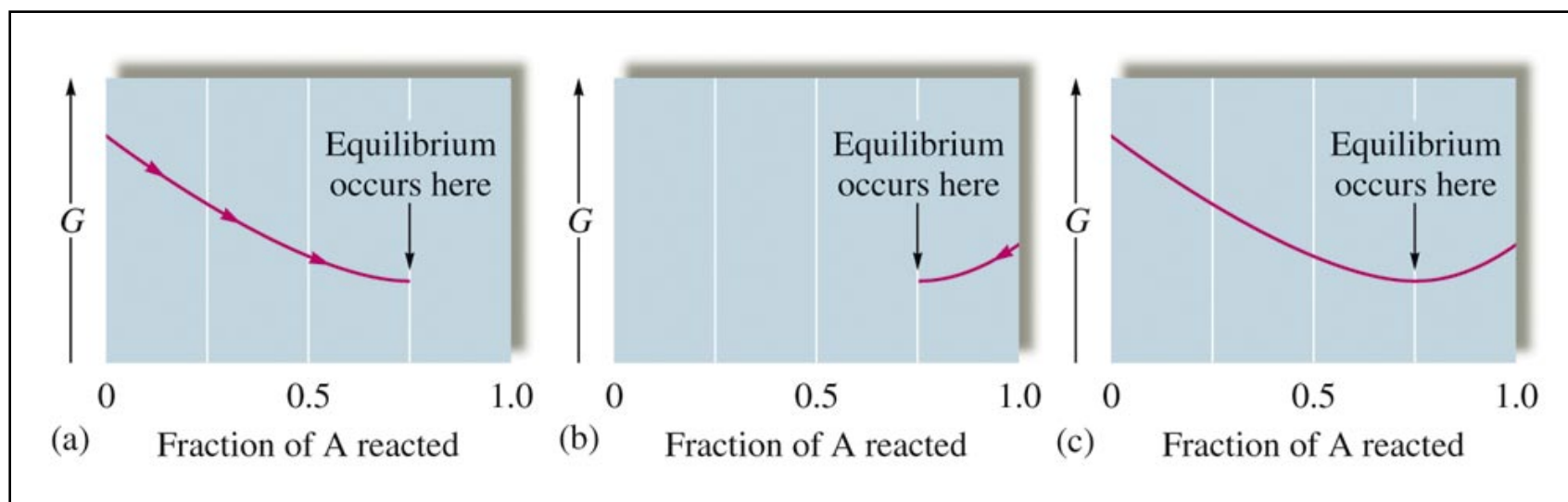


Table 16.6 Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

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ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

QUESTION

Sulfur dioxide often forms when the sulfur in coal combines with oxygen. Then SO_2 is converted to SO_3 (a problem involved with acid rain formation) via the following reaction:



If the reaction were allowed to come to equilibrium at 145°C in a closed container, what would be the value for the equilibrium constant?

$$\text{Answer} = 5.67 \times 10^{17}$$

QUESTION



Calculate the equilibrium constant for the formation of ferric oxide (rust), using standard enthalpy and entropy values.

$$K = e^{601}$$